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Reduction of the Solubility of Enamel Surfaces.[1]

By

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Survey of the Literature.

Hydroxyl apatite is the principal substance to go into solution during acid attack of the dental enamel: this is the conclusion reached from literature by the author in a previous work. Experimental data presented in the work further support this conclusion (ERICSSON 1949). It would seem, however, that the solubility of enamel apatite may vary and also be actively influenced, which is quite reasonable in view of our knowledge of the apatite crystal and its possibilities of substitution. It would appear, in the first place, that Ca and OH groups in the hydroxyl apatite molecule, $Ca_5(PO_4)_3OH$ can be replaced without any great alteration of the lattice constants, the former by Pb and Mg and possibly by other metals as well (KLEMENT 1938, MCCONNELL 1938, THEWLIS 1940), and the latter by Cl and F, which often constitute part of the molecule of mineral apatites. It would seem that the OH group could be readily replaced by F without decomposition of the crystal. The reason for this is most likely that the OH group closely resembles the F-atom in atomic weight, nuclear charge and electron configuration (KOVALIV and HELD 1947). The reactivity is so great that the mineral calcium phosphate (which is mostly crystallised as the apatite)

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[1] This investigation forms part of co-ordinated work on dental caries sponsored by the Swedish Medical Research Council through its Sub-committee for Caries Research.

could be used as a filter for the removal of fluorine from drinking water of high fluorine content (McINTIRE and HAMMOND 1938, ADLER, KLEIN and LINDSAY 1938).

The discovery of a connection between a high fluorine content of drinking water and low caries frequency suggested the hypothesis that a fluorine substitution of the apatite molecules in the surface-layer of the dental enamel reduces the solubility. That a permanent ion exchange does take place between the surface-layer of the enamel and the mouth fluids is a fact well-established, especially by several tests with radioactive phosphorus. A still more pronounced uptake of the reactive fluorine on contact with the enamel surface was to be expected, and VOLKER, HODGE and collaborators (1940) were in fact able to establish this with the radioactive isotope F^{18}. It was later shown by means of X-ray spectrographic technique that not only the intact surface in situ (HOLAGER and SYRRIST 1948) but also the plane-polished enamel surface (GEROULD 1945) could be converted in part to CaF_2 by contact with fluoride solutions.

Both fluorine-substituted apatite, $Ca_5(PO_4)_3F$, and CaF_2 are considered less soluble than the hydroxyl apatite. This is certainly true of the CaF_2 (SEIDELL's handbook 1940); concerning fluorapatite no previous investigations of a precise nature seem to have been reported.

Reduction of the solubility of the enamel surface is not, however, the only conceivable mechanism for effecting caries-reduction by fluorine. It is well-known that fluorine is an enzyme poison which inhibits phosphorylization and carbohydrate degradation and it might therefore be supposed that some such effect plays a part in this case. BIBBY and VAN KESTEREN (1940) found that two parts per million of sodium fluoride in an otherwise suitable substrate reduced the acid-production of the mouth bacteria and that addition of fluorised dentin inhibited the acid-formation in vitro more than normal dentin. JAY and ARNOLD (in: Moulton, Dental caries and fluorine, 1946) produced experimental data which denote a smaller number of caries-indicating lactobacilli in the saliva of subjects of fluorine-rich regions and HODGE and SOGNNAES (ibid.) assumed that a relatively high concentration of absorbed or bonded fluorine in the outer surface-layer of the enamel might have a local enzyme-inhibiting effect.

We shall only consider here, however, the solubility-reducing effect of fluorine. This has mainly been studied up to the present

Table 1.

Author	Year	Tested ions											
		F^-	Pb^{++}	Ag^+	Cu^{++}	Sn^{++}	Th^{++++}	UO_2^{++}	In^{+++}	Be^{++}	Yt^{+++}	Ba^{++}	$C_2O_4^{--}$
Hill & Arnold	1937			+									
Volker	1939	+											
Buonocore & Bibby	1945	+	+	(+)									
Rae & Clegg	1945	+											+
Phillips & Muhler	1947	+											
Muhler & Van Huysen	1947	+	+	+	+	+	+	+					
Bibby	1947	+			+								
Kovaliv & Held	1947	+											
Lazansky	1947	+	+						+	+	+		
Rae & Clegg	1948	+	+	+								+	+
Manly & Bibby	1949	+	+		+	+	+		+	+	+		+

with pulverised dental enamel. A number of workers have investigated the loss of weight in given acid solutions of pulverised dental enamel, with and without previous treatment with fluorine and other ions. Their results have been summarized in the table given above (Table 1), in which + signifies reported solubility-reducing effect.

The most recently published investigations of Manly and Bibby covering a great many ions in addition to those which appear in the tables, show that there is a large number with a greater solubility-reducing effect than the fluoride ion, when their concentrations correspond to that of the fluoride (0.1 % NaF). To these active ions belong the complex fluoroborate ion together with gallium, yttrium, lead, indium, beryllium, cerium, bivalent tin and others. Buonocore and Bibby found a particularly strong effect with lead fluoride and Muhler and Van Huysen found that Sn^{++}, Pb^{++} and UO_2^{++}, in the order mentioned, were more effective than F^-.

Now it might of course be questioned whether these results from experiments with pulverised enamel can tell us anything of the behaviour with intact enamel surfaces. This question has been discussed by Brudevold (1948) and others who studied the phosphate solubility of different enamel surfaces. Brudevold determined the amounts of phosphorus dissolved from round surfaces, 4 mm in diameter during ten minutes shaking in an acetate buffer of pH 4 at a temperature of 37°C. He found variations between different teeth and between different surfaces of the same tooth. Temporary teeth and uninterrupted teeth were on the average more soluble than interrupted, permanent teeth. Ground surfaces were more soluble than intact surfaces.

Original Investigations.

First Experimental Series.

The investigations presented here are intended to give an insight into the possibilities of influencing chemically the rate of dissolution of intact enamel surfaces.

Method.

Intact permanent teeth, usually cuspids or bi-cuspids, were, after removal of calculus and washing with distilled water, split lengthways and as nearly as possible into similar halves. All surfaces except the outer enamel ones were covered first with a layer of varnish and then with wax. The test solution was applied by rubbing with cotton wool for five minutes to one of the halves, the other being used as a control. Each half was then treated with 10 ml of a 0.001 N HCl solution in a rotating glass vessel for two hours at 37°C; the solution being at the same time 0.025 molar NaCl. The solutions were tested for pH and analysed for inorganic phosphate and calcium. The same methods of analysis were used as in previously published work (Ericsson 1949).

Controls showed that no phosphorus or calcium dissolved from teeth which were completely covered by the varnish and wax. The solutions used for painting were chosen on the basis of published data on solubility-reducing ions: they were:

1. sodium fluoride, 5 %,
2. sodium fluoride, 0.1 %,
3. stannous fluoride, fluorine-content corresponding to 2 % NaF,
4. sodium fluoride, 2 % + $^1/_{10}$ equivalent stannous chloride,
5. stannous fluoride, F-content corresponding to 2 % NaF,
6. lead fluoride, saturated solution,
7. calcium fluoride, saturated solution,
8. stannous chloride, Sn-content corresponding to solution 3,

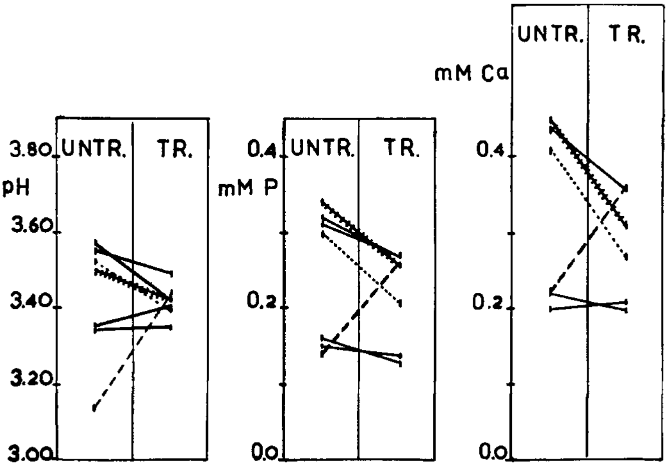


Diagram 1. Sodium fluoride, 5 %.

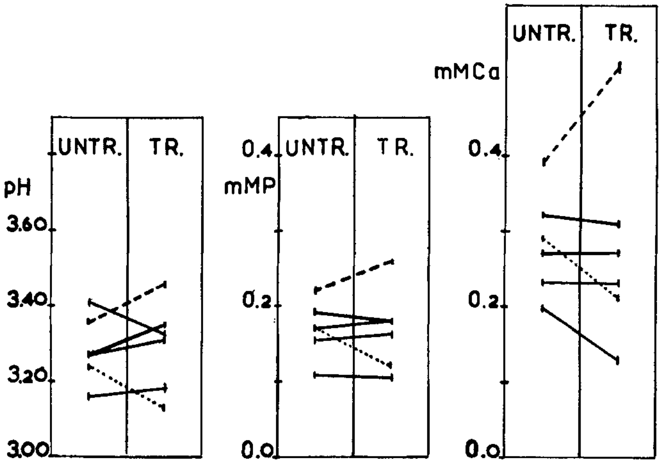


Diagram 2. Sodium fluoride, 0.1 %

9. lead acetate, 1 % solution,
10. hydrochloric acid, 0.001 N,
11. copper sulphate, 2 %,
12. ammonium oxalate, 5 %,
13. uranyl acetate, 2 %.

All percentages are reckoned without water of crystallization. Stannous fluoride solutions were prepared by mixing stannous chloride and sodium fluoride.

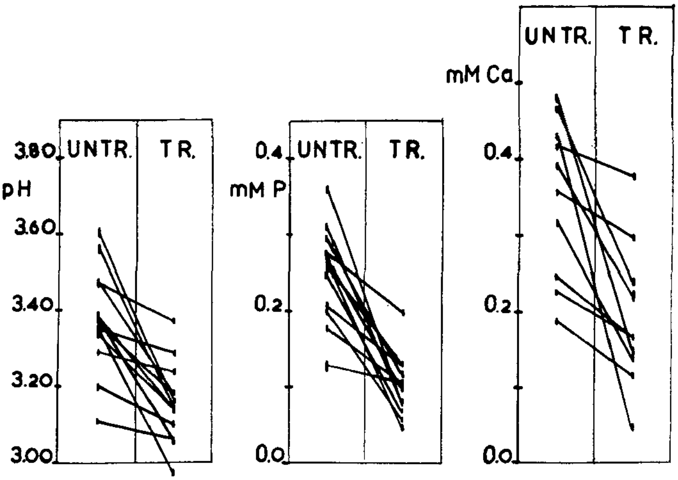


Diagram 3. Stannous fluoride, fluorine content corresponding to 2 % NaF.

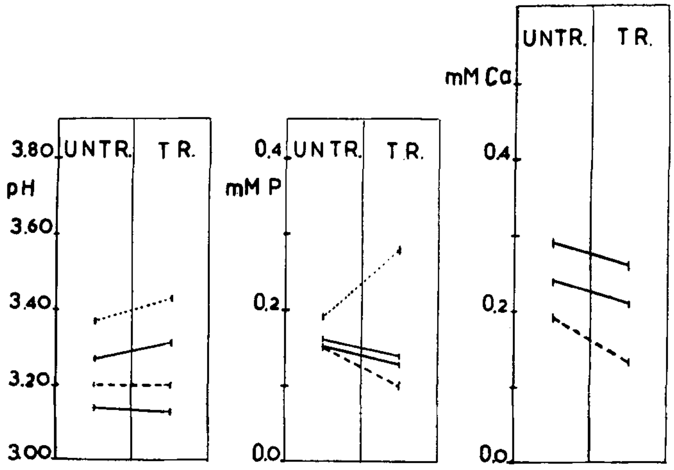


Diagram 4. Sodium fluoride, 2 %, + 1/10 equivalent stannous chloride.

Stannous chloride and lead acetate, in the second of the above groups, were included to test the effect of Sn^{++} and Pb^{++} in the absence of F^-. Since the solutions, which contained $SnCl_2$, were strongly acid (solution 3: pH = 2.65; solution 5: pH = 3.11) it was possible that the acid itself might have produced some effect. For purposes of comparison, therefore, a number of tests were included with 0.001 N hydrochloric acid, whose pH-value lay in the region of that of the $SnCl_2$ solution.

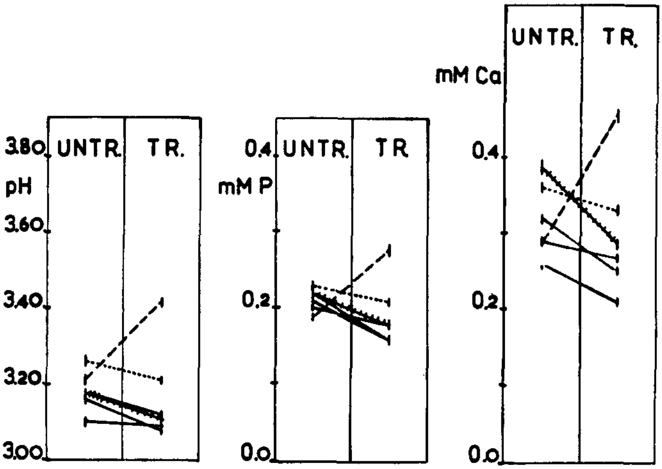


Diagram 5. Stannous fluoride, F-content corresponding to 2 % NaF.

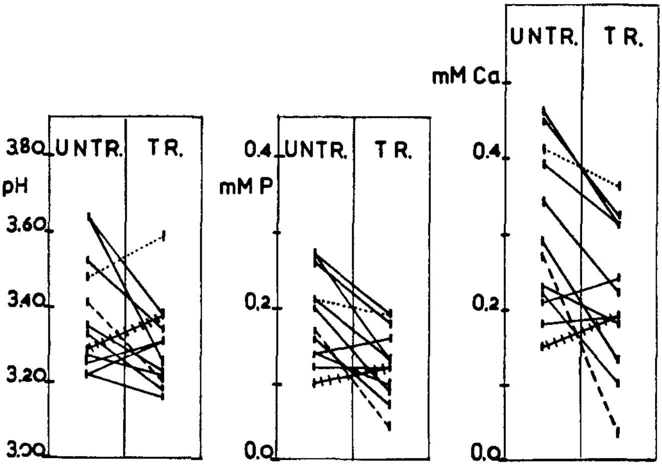


Diagram 6. Lead fluoride, saturated solution.

Results.

The analysis results have been summarized in diagrams 1—13, where the amounts of phosphorus and calcium dissolved are given in millimolar concentration of the test solutions. "Untr." = untreated surface, "tr." = treated surface. Values from related tooth halves are joined in the diagrams by straight lines, the direc-

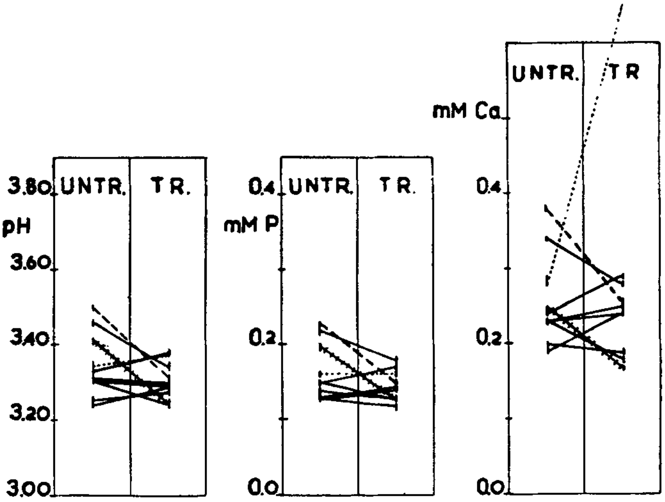


Diagram 7. Calcium fluoride, saturated solution.

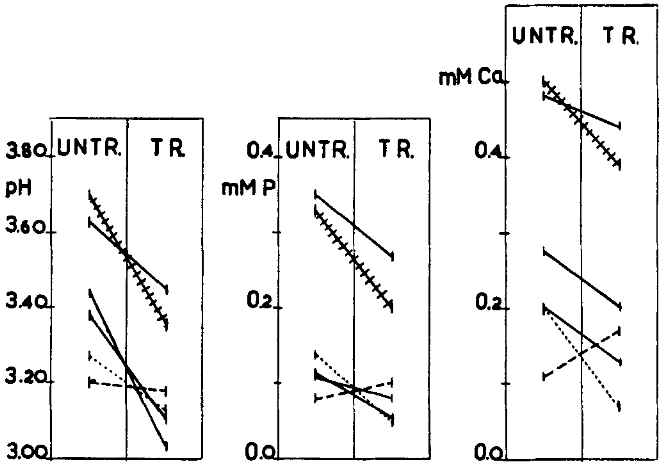


Diagram 8. Stannous chloride, Sn-content corresponding to solution 3, diagram 3.

tions of which indicate the tendency of the result. In those cases where characteristic differences could be read off between treated and untreated halves of the same tooth, the joining lines for each test have been marked in such a way as to make it possible to compare Ca-dissolution, P-dissolution and the resulting pH-value for individual teeth.

The molar ratios between the dissolved amounts of phosphorus

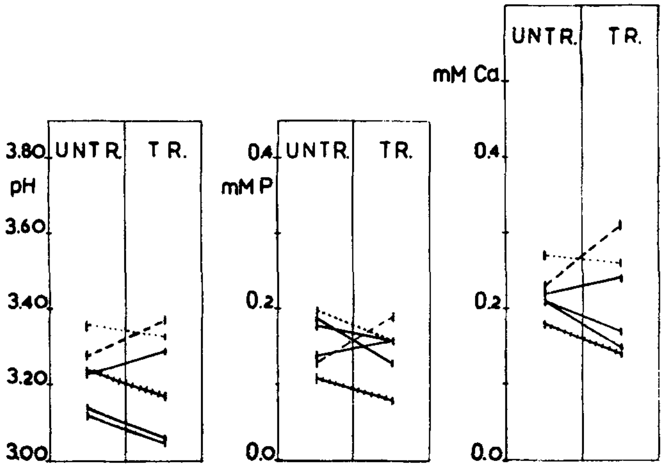


Diagram 9. Lead acetate, 1 % solution.

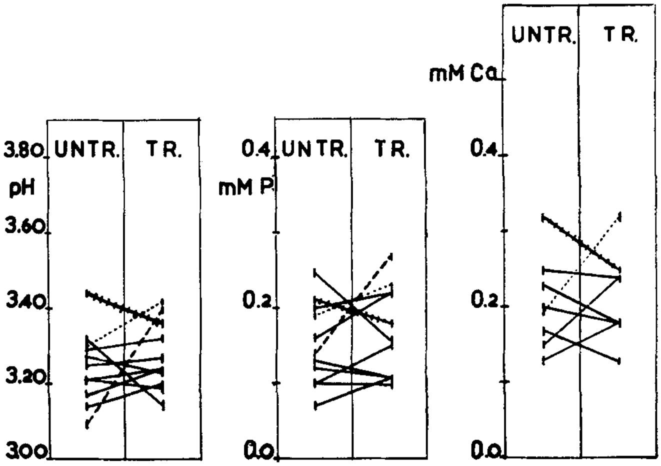


Diagram 10. Hydrochloric acid, 0.001 N.

Table 2.

Molar P:Ca ratios after influence of different ions.

Solution		1	2	3	4	5	6	7	8	9	10	11	12	13
P/Ca	Min.	0.62	0.49	0.34	0.54	0.62	0.40	0.25	0.39	0.57	0.54	0.68	0.62	0.44
	Mean	0.72	0.64	0.61	0.64	0.66	0.60	0.59	0.54	0.72	0.72	0.75	0.69	0.52
	Max.	0.83	0.82	0.97	0.74	0.75	1.56	0.78	0.71	0.96	0.84	0.88	0.85	0.59

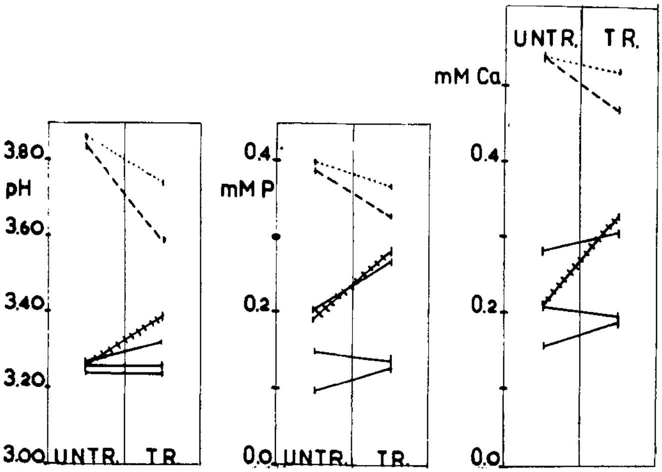


Diagram 11. Copper sulphate, 2 %.

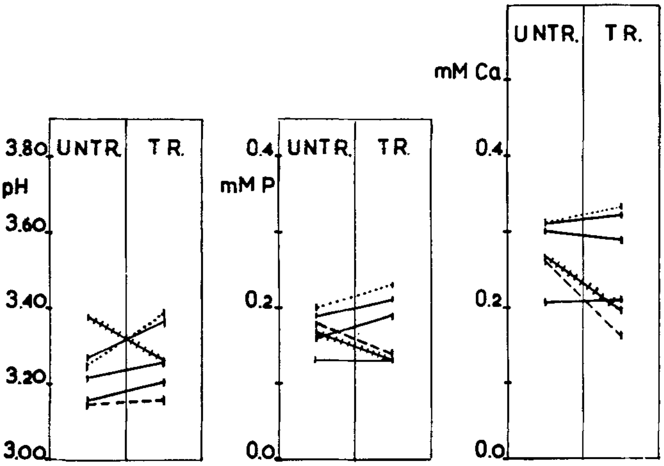


Diagram 12. Ammonium oxalate, 5 %.

and calcium after treatment with the various ions were calculated and set out in Table 2. From untreated tooth surfaces there was dissolved on the average about 0.12 mg calcium and about 0.06 mg phosphorus; the molar P:Ca ratio was 0.67 ± 0.01.

Discussion of the Results.

The molar ratio of 0.67 between the quantities of phosphorus and calcium dissolved from the unchanged enamel surfaces lies

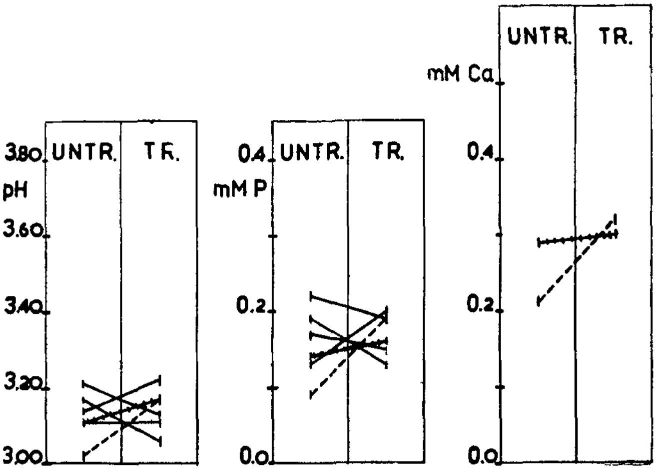


Diagram 13. Uranyl acetate, 2 %.

near the P:Ca ratio which various investigators found for the enamel's total mass (0.64 according to Armstrong and Brekhus 1937).

No significant deviation from this ratio is observable for the different ions used.

With change of the amounts dissolved after treatment with the different ions an obvious parallel is found to exist between quantities of dissolved phosphorus and calcium and the degree of neutralization of the acid test solution. Each of the analysed factors P, Ca and pH therefore gives us information of the direction and magnitude of the change, a fact that can be of practical value. By reason of its simplicity, analysis of the pH-value alone permits mass investigations; by its greater sensitivity, analysis of phosphorus concentration allows investigations on a microscale, which more nearly approaches the conditions in vivo.

The most pronounced and significant decrease in the rate of dissolution was obtained with the strongest stannous fluoride solution. That the Sn^{++} ion is, in this case, the most powerful factor is probable for several reasons: the weaker SnF_2-solution shows in six cases out of eight the same tendency; the pure $SnCl_2$ solution has in five cases out of six greatly reduced the dissolution and the neutralization of the acid; HCl solutions of corresponding acidity have not given a definite result in any direction.

Lead fluoride shows the next strongest effect: in nine cases out of twelve there was decreased dissolution. The Pb^{++} ion in 1 % lead acetate has in four cases out of six given reduced dissolution.

Of the remaining fluorides tested none has given any significant effect even though 5 % NaF in most cases reduced the dissolution.

The experiments with Cu^{++}, UO_2^{++} and $C_2O_4^{--}$ do not show any clear trend.

Second Experimental Series.

These investigations were intended as a study of the effect exerted by some especially interesting ions on the rate of dissolution of the intact enamel surface under chemical conditions which will more resemble those in the oral cavity.

Method.

The same technique was used as in the first series of experiments with the exception that the acid test solutions consisted of acetate buffers or ammonium chloride solutions with an initial pH of about 5, and that only the dissolved phosphate was analysed. The ions whose effect was being investigated, were fluorine, lead, tin and silver.

The lead ion in particular seemed to be of interest because according to previous investigators it considerably reduces the rate of dissolution of the enamel surface and because taste (of lead acetate) and toxicity should not prevent local application in vivo. The pH value of 5 for the acid test solutions was chosen because it has been shown that such a pH level may exist in the oral cavity (STEPHAN 1940), and because the rate of dissolution of the enamel phosphate is easily determined at that value. In some of the experiments with the lead ion the test solution used was ammonium chloride, of pH about 5.3, through which was bubbled during the experiment a mixture of 6.1 % CO_2 in air. This arrangement was chosen because an hypothesis put forward by BIBBY (1948) suggests that ammonium ions in the oral cavity might be able to increase the solubility of any lead compounds in the enamel surface. The concentration of the CO_2 used for bubbling approximately corresponded at 37°C to the physiological CO_2 pressure.

In one of the following series of tests the teeth were, before cleaving, exposed for 24 hours to an acetate buffer of pH 5.0, by which the enamel surfaces were slightly etched.

Finally two series were devoted to the investigation of the effect of Sn^{++} and Ag^{+} ions.

The following tests were carried out:

1. Comparative tests on the effect of saturated lead fluoride solution and sodium fluoride and lead acetate solutions of corresponding concentration. Test solution; 0.2 M acetate buffer, pH 5.0.

a) Saturated PbF_2 (= approx. 2.6 mM).
b) 5.2 mM NaF.
c) 2.6 mM $PbAc_2$.

2. Tests with stronger sodium fluoride and lead acetate solutions. Test solution: 0.2 M acetate buffer pH 5.0.

a) 0.1 % NaF (= 25 mM).
b) 1 % $PbAc_2$ (= approx. 30.7 mM).

3. 2.6 mM lead acetate. Test solution: 0.2 M ammonium chloride, pH 5.3, bubbled with 6.1 % CO_2 in air.

4. The same as (3) but with enamel surfaces treated before the test with 0.2 M acetate buffer pH 5.0 for 24 hours.

5. Stannous chloride, 25 mM (= $^1/_{10}$ of the concentration of solution 8, first experimental series). Test solution: 0.2 M acetate buffer, pH 5.0.

6. Silver nitrate, 1 %. Test solution: 0.2 M acetate buffer, pH 5.0.

Results.

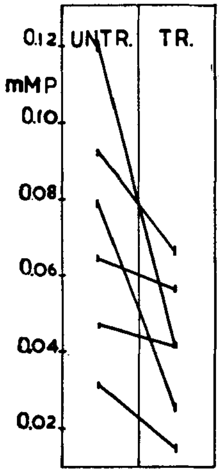
The analysis results are summarized in Diagrams 14—22 where the dissolved phosphorus is given in the millimolar concentration of the test solutions in the same way as in the first series.

Discussion of the Results.

Treatment of the enamel surface with lead fluoride led in each individual test to reduced phosphate dissolution.

In the tests for fluorine and lead separately the fluorine ion gave no clear result, whether it was in that concentration which corresponded to saturated PbF_2 or of greater concentration.

The lead ion has in a definite majority of cases given reduced dissolution of the phosphate under different experimental condi-



Digram 14. Lead fluoride, saturated solution (2nd series, 1 a).

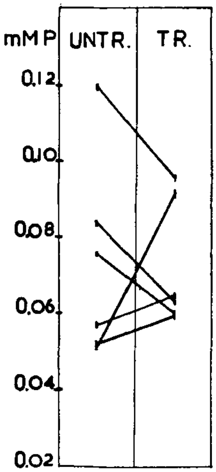


Diagram 15. Sodium fluoride, 5.2 mM (2nd series, 1 b).

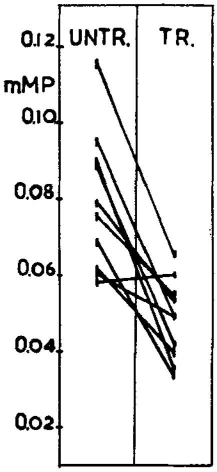


Diagram 16. Lead acetate, 2.6 mM (2nd series, 1 c).

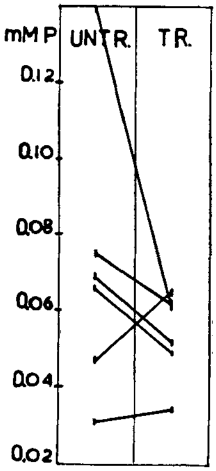


Diagram 17. Sodium fluoride, 0.1 % (2nd series, 2 a).

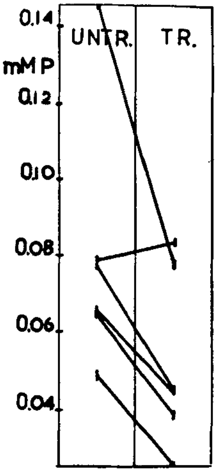


Diagram 18. Lead acetate, 1 % (2nd series, 2 b).

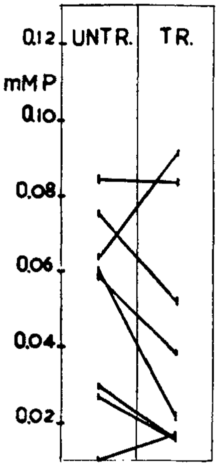


Diagram 19. Lead acetate, 2.6 mM (2nd series, 3).

tions. No difference could be distinguished between the effect of varying concentrations of lead acetate. The effect of the ammonium ion on the dissolution of phosphate after treatment with lead is uncertain.

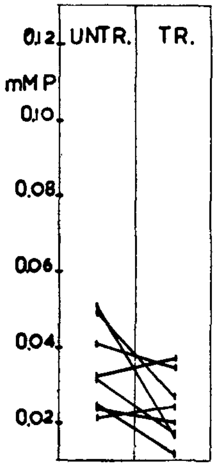
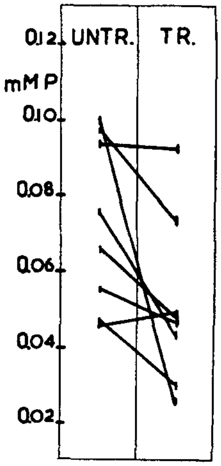


Diagram 20. Lead acetate, 2.6 mM (2nd series, 4).



Diagrgm 21. Stannous chloride, 2.5 mM (2nd series, 5).

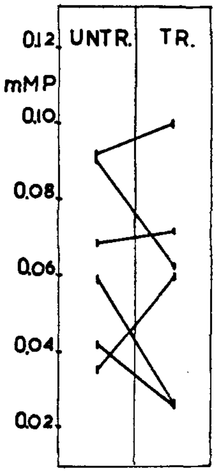


Diagram 22. Silver nitrate, 1 % (2nd series, 6).

Previous treatment of the enamel surfaces with a buffer solution of pH 5 seems to have shifted the rate of dissolution to a low and fairly steady level in subsequent tests with ammonium chloride of pH 5.3. It would appear natural, on theoretical grounds, that an acid fluid would, by attacking the most soluble constituents, reduce the rate of dissolution of the surface structure in the subsequent less acid liquid.

The weak stannous chloride solution, which was tested in the test series number 5 has in most cases afforded an obviously reduced dissolution of phosphate. With silver nitrate no clear effect was obtained.

Before one attempts to draw conclusions from the solubility tests in vitro concerning the possibility of influencing the carious enamel dissolution, one should be clear in one's mind on the differences between the acid solutions used in the tests and the acid environment of the predilection surfaces of the tooth. One of the most important factors in this respect will be the concentration of free ions. In the acid-forming plaque one must reckon with considerable concentrations of calcium and phosphate ions which retard, to a great extent, the dissolution of the corresponding ions from the enamel surface. On the other hand subsequently substituted ions in the enamel apatite, such as F^-, Sn^{++} or Pb^{++}, would probably on the whole lack counterparts in the liquid phase. This might possibly explain the reports that the clinical application of PbF_2 has not, up to the present, resulted in any caries-reduction (Bibby, de Roche and Wilkins 1947; Galagan and Knutson 1947).

Third Experimental Series.

The acid solutions analysed in the first experimental series were all very unsaturated with respect to hydroxyl apatite, if the degree of saturation is calculated from Bjerrum's and Schmidt-Nielsen's formulae.

Bjerrum gave (1936) the following formula for the solubility of the hydroxyl apatite: $5p\,[Ca] + 3p\,[HPO_4] - 4pH = 7.5 - 16.5\sqrt{\mu}$, where $[Ca]$ = the calcium ion concentration and $[HPO_4]$ = the hydrophosphate ion concentration at saturation, and μ = the ionic strength.

The formula is valid at equilibrium, reached from the unsaturated side, at 37°C.

Schmidt-Nielsen showed (1946) that the degree of saturation of hydroxyl apatite in a solution, *i. e.* the ratio between the obtaining quantity of apatite in the solution and the quantity dissolved at saturation, can be calculated from the formula:

$$\log n = \frac{pL - pI}{9} \quad \text{where } n = \text{degree of saturation,}$$

$$pL = 7.5 - 16.5\sqrt{\mu}$$

$$pI = 5p\,[Ca] + 3p\,[HPO_4] - 4pH;$$

μ, $[Ca]$ and $[HPO_4]$ signifying respectively ionic strength and calcium and hydrophosphate ion concentrations according to the analysis of the solution.

The derivation of these formulae is given in the cited works by Schmidt-Nielsen (p. 62) and Ericsson (p. 30).

According to these formulae, the calcium and phosphorus concentrations obtained in the test solutions of the first experimental series correspond to saturation somewhere in the pH-range 6—7, while the pH-value of the test solutions had risen only some tenths above pH 3. The presence of the carbonic acid system further increases the solubility of the apatite in the pH region above 5 (Ericsson 1949), a point of some significance here on account of the carbonate content of the dental enamel.

Since the test solutions were thus very unsaturated, their calcium and phosphorus content indicates the initial *rate of dissolution.* From this conception one should distinguish *solubility,* which denotes the amount of solid substance dissolved at complete saturation, Previous literature has not always kept this distinction clear. It is also obvious that the rate of dissolution is dependent on the absolute solubility to a great extent.

To illustrate the effect of the fluoride ion on the solubility of hydroxyl apatite some equilibrium experiments were carried out with synthetic hydroxyl apatite and pulverised dental enamel which were exposed for a short time to sodium fluoride solutions. For comparison the same equilibrium experiments were performed with fluorapatite and calcium fluoride.

Method.

A. Substances tested for solubility.

1. Synthetic hydroxyl apatite, a fine-grain precipitate (description of precipitation: ERICSSON 1949, p. 47).

2. 200 mg of the same apatite, shaken for one minute with 5 ml 5 % NaF solution (pH = 7.6); washed three times, dried at 110°C.

3. 200 mg of the same apatite, shaken for one minute with 5 ml of a mixture of one part 5 % NaF solution to two parts 30 % H_2O_2 solution (pH = 5.2); washed three times, dried at 110°C. The NaF-H_2O_2 mixture was used because a similar one was considered by a previous author to be more effective than a pure NaF solution (BIBBY 1947).

4. Dental enamel, mixed from several teeth, pulverised and passed through a sieve no. 100 (inner width of mesh 0.06 mm).

5. The same dental enamel, treated with 5 % NaF as in (2) above.

6. The same dental enamel, treated with NaF-H_2O_2 solution as in (3) above.

7. Synthetic fluorapatite, prepared in the same way as the hydroxyl apatite in (1) above, but with equivalent amount of NaF added with the phosphate solution on precipitation.

8. Calcium fluoride, analytically pure commercial preparation.

B. Solution for equilibrium tests:

$\begin{cases} 0.0025\ \text{N hydrochloric acid} \\ 0.025\ \text{M sodium chloride.} \end{cases}$

C. Equilibration: 20 mg powder rotated for 8 hours at 37° C with 20 ml solution, and then analysed according to the technique previously referred to.

Results.

The analysis results appear in Tables 3—5. Calcium and phosphorus are given in millimolar concentrations; n is the degree of saturation calculated from the analyses.

Table 3.

Preparation	Synthetic $Ca_5(PO_4)_3OH$		
Treatment	1 Unchanged	2 Treated with 5 % NaF	3 Treated with NaF + H_2O_2
pH	5.65	4.83	4.62
P	0.95	0.84	0.88
Ca	1.68	0.56	1.61
n	1.1	0.14	0.17

Table 4.

Preparation	Pulverised enamel		
Treatment	4 Unchanged	5 Treated with 5 % NaF	6 Treated with NaF + H_2O_2
pH	5.75	4.80	4.68
P	0.99	0.79	0.85
Ca	1.56	1.62	1.73
n	1.28	0.23	0.16

Table 5.

Preparation	7 Fluorapatite	8 Calcium fluoride
pH	4.70	2.92
P	1.16	—
Ca	1.72	0.82
n	0.22	—

Discussion of the Results.

A degree of saturation of 1.1 was obtained from the solubility test with unchanged hydroxyl apatite. The deviation from the theoretically expected value of 1.0 lies well within the normal range of variation for this salt's solubility.

The corresponding value for unchanged dental enamel is 1.28. This high value may have its explanation in the carbonate content of dental enamel which raises the apatite's solubility at the pH level of this experiment, 5.75 (ERICSSON 1949).

The values for the fluorine-treated preparations show that these are very unsaturated with regard to hydroxyl apatite at the end of the equilibration, with n-values between 0.14 and 0.23. On studying the analysis figures it is found that this is mainly dependent on the fact that the pH-values lie about one unit lower than in the corresponding tests with untreated preparations. The quantities of dissolved calcium and phosphorus show, on the other hand, no great difference except for preparation 2, whose calcium dissolution is very low.

If the solubilities of the fluorine-treated preparations and the synthetic fluorapatite are compared, it is found in three cases out of four that there is a striking agreement: a dissolution of calcium and phosphorus of the same magnitude as from the unchanged hydroxyl apatite but a low final pH.

The small amount of calcium dissolved in the case of preparation 2 might possibly be explained by considering that the fluorine concentration for some reason became higher in this solution whereby the low solubility product for CaF_2 reduced the calcium concentration. In the equilibrium test with pure CaF_2 it is seen that the calcium concentration at pH 2.92 is as low as 0.82 mM.

The conclusion we are entitled to draw seems to be that the dental enamel which is exposed for a short time to fluoride ions changes its solubility in a direction towards that of the pure fluorapatite. The data presented here do not in themselves give any support for the idea that this change would reduce the solubility since equally large amounts of calcium and phosphorus were dissolved from the fluorapatite and the fluorised enamel by a given quantity of acid as from the unaffected enamel.

It might rather be thought that only a more intense effect of the fluorine with formation of a surface layer of CaF_2 would be able essentially to reduce the solubility and the rate of dissolution. GEROULD's investigations point in this direction (loc. cit.): more prolonged effect of fluorine converted pulverised enamel as well as a polished enamel surface to CaF_2. GEROULD reports, moreover, a certain difference in rate of dissolution between hydroxyl apatite and fluorapatite.

Summary.

In a survey of literature an account is given of earlier experiments on ionic exchange with effect of decreasing the rate of dissolution of pulverised enamel. Original investigations are presented regarding the corresponding possibility of influencing the intact enamel surface and also with regard to the solubility of fluorised hydroxyl apatite and fluorised enamel powder.

Principal results:

1. The molar ratio between the amounts of phosphate and calcium dissolved in acid lies in the neighbourhood of the same ratio for the total mass of enamel. This holds for dissolution from intact enamel as well as from enamel surfaces affected by active ions.
2. In the case of dissolution of enamel in unbuffered acid there is a direct relationship between dissolved phosphorus and calcium and the resulting pH value. This connection enables each of these factors to be used as an indicator of the rate of dissolution. In buffered, slightly acid liquids the phosphate dissolution is a convenient indicator.
3. Under the conditions of the tests, the stannous and lead ions have shown a more marked inhibition of solubility on enamel than the fluoride ion. No distinct effect was obtained with copper, silver, oxalate, or uranyl ions.
4. In the case of fluorine action of short duration on synthetic hydroxyl apatite and pulverised dental enamel, the solubility changes in a direction towards that of pure fluorapatite.
5. In equilibrium experiments with fluorapatite and hydroxyl apatite approximately equal quantities of phosphorus and calcium were dissolved in both cases, but the dissolved fluorapatite neutralized the acid solution to a considerably less extent than the hydroxyl apatite.

Résumé.

Dans un résumé de la littérature on a décrit brièvement les expériences antérieures d'échanges ioniques dont l'effet diminue la vitesse de dissolution de l'émail pulvérisé. Les investigations faites par l'auteur se rapportent à la possibilité correspondante d'influencer la surface intacte de l'émail et également à la solubilité de l'hydroxylapatite fluorisé et de l'émail en poudre fluorisé.

Résultats principaux:

1. Le rapport entre les taux molaires de phosphate et de calcium dissous dans l'acide est voisin du rapport correspondant de la masse totale de l'émail. Ceci est valable pour la dissolution avec non seulement l'émail intact mais encore avec les surfaces d'émail affectées par les ions actifs.
2. Pour une dissolution d'émail dans un acide nontamponné il existe une relation entre les quantités de phosphore et de calcium dissous et le pH résultant. Cette relation permet l'utilisation de chacun de ces facteurs comme indicateur de la vitesse de dissolution. Dans un liquide tamponné et faiblement acide le phosphate dissolu est un indicateur convenable.
3. Dans les conditions des essais, les ions Sn^{++} et Pb^{++} ont accusé une diminution de dissolution plus forte que les ions F^{-}. On n'a obtenu aucun effet décisif avec les ions de cuivre, d'argent, d'oxalate et d'uranyl.
4. Lorsque le fluor agit sur l'hydroxylapatite synthétique et sur l'émail dentaire pendant peu de temps seulement, la solubilité change dans la direction vers celle de la fluorapatite pure.
5. Dans les expériences d'équilibre tentées avec la fluorapatite et l'hydroxylapatite on a trouvé que les quantités de phosphore et de calcium dissous sont à peu près égales dans les deux cas, mais la neutralisation de la solution acide a été beaucoup moins forte pour la fluorapatite que pour l'hydroxylapatite.

Zusammenfassung.

In einer Literaturübersicht bespricht der Verfasser frühere Untersuchungen über solchen Ionenaustausch, welcher die Auflösungsgeschwindigkeit pulverisierten Zahnschmelzes herab-

setzt. Eigene Untersuchungen werden vorgelegt über die entsprechende Möglichkeit, die intakte Schmelzfläche zu beeinflussen, und auch über die Löslichkeit des fluorbehandelten Hydroxylapatites und des fluorbehandelten Schmelzpulvers.

Hauptergebnisse:

1. Das molare Verhältnis zwischen den in Säure sich auflösenden Mengen von Phosphor und Kalzium liegt in der Nähe desselben Verhältnisses für die ganze Masse des Schmelzes. Dies gilt bei Auflösung sowohl von der intakten Schmelzfläche als von Schmelzflächen, die aktiven Ionen ausgesetzt worden sind.
2. Bei Schmelzauflösung in ungepufferter Säure besteht eine direkte Relation zwischen den gelösten Mengen von Phosphor und Kalzium und dem resultierenden pH-Wert. Diese Relation ermöglicht den Gebrauch jeder dieser Faktoren als Indikator der Auflösungsgeschwindigkeit. In gepufferten, schwach sauren Flüssigkeiten ist die Phosphatauflösung ein geeigneter Indikator.
3. Unter den angewendeten Versuchsbedingungen haben die Stanno- und Bleiionen eine stärkere löslichkeitsvermindernde Wirkung gezeigt als der Fluoridion. Mit Kupfer-, Silber-, Oxalat- oder Uranylionen wurde keine deutliche Einwirkung erhalten.
4. Bei kurzdauernder Fluoreinwirkung auf synthetischem Hydroxylapatit oder pulverisiertem Zahnschmelz nähert sich die Löslichkeit dieser Substanzen der des reinen Fluorapatites.
5. In Gleichgewichtsversuchen mit Fluorapatit und Hydroxylapatit wurden in beiden Fällen etwa diselben Mengen von Phosphor und Kalzium aufgelöst, der gelöste Fluorapatit neutralisierte aber die saure Flüssigkeit in einem bedeutend niedrigeren Grade als der Hydroxylapatit.

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